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(19)

(54) METHOD OF REMOVING AN ELECTRODEPOSITED METAL FROM A CATHODE

(71) We Imperial Metal Industries (Kynoch) Limited, a British Company, of Kynoch Works, Witton, Birmingham B6 7BA, and IMI Refiners Limited, a British Company, of Darlaston Road, Walsall, Staffordshire do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a method of removing an electrodeposited metal from a cathode.

In the electrorefining of metals, particularly of copper, it is common practice to deposit on a copper or stainless steel cathode plate having a greased surface, a layer of metal of little more than foil thickness. This thin deposit is stripped off manually and is used as a starter sheet or cathode for the formation of a heavy deposit of metal.

The difficulties of stripping the thin deposit and the associated damage to the cathode plate, together with the lack of resistance to liquid surface level corrosion, have led to the development of titanium cathode plates to replace the copper cathode plates. In a further development of electrorefining, it is known to deposit a thick layer of copper onto the titanium cathode plates without the use of a thin copper starter sheet.

Removal of a thick deposit is difficult and manula or complex mechanical methods are employed, which increase handling costs, and adaptations of the titanium plates have been proposed to facilitate removal of the deposit, including masking of the edges of the plates with a non-conductive edging such as plastic.

According to the invention, a method of removing an electrodeposit of metal adhering to a flat cathode plate of a metal of dissimilar coefficient of thermal expansion includes the steps of subjecting the deposit and the cathode plate to a temperature change thus creating a thermal expansion or contraction differential between the deposit and the cathode plate, whereby the resulting stresses generated at the interface between the deposit and the cathode plate are sufficiently great to reduce adhesion between the deposit and the cathode plate.

Preferably the differential is produced by cooling, for example, by quenching, at or below ambient temperature, but heating, eg immersion in water at or near the boiling point, is also effective.

After cooling to the desired temperature, the deposited and plate may be reheated to reduce adhesion further. Separation may be complete after either the quenching step or the heating step but in some cases more than one quenching and reheating may be required. After the initial heating step, the cathode plate and deposit may be quenched or otherwise rapidly cooled.

Preferably the temperature is reduced about 60°C by quenching in a cold liquid bath from the temperature of the electrolyte, usually about 60°C. Such a bath may be water-based containing a freezing point depressant, such as brine, chilled to about 0°C. Liquid oxygen or nitrogen may be used but offer no outstanding advantages relative to their cost.

Alternatively, cooling in cold air, ie at or below ambient temperature, or dry ice, ie solid CO_2, may be employed.

The deposit which may be about ½ inch thick on each side of a titanium cathode plate, after removal from the electrolyte is conventionally rinsed in cold water to remove electrolyte prior to stripping manually. In a preferred manner of carrying out the process according to the invention, the normal procedure is modified in that the cathode plate and the deposit are transferred from the electrodeposition bath to an environment of 60 - 70°C, eg immersed in hot water, in order to retain the temperature of the electrolytic bath during rinsing and then quickly transferred to the chilling bath. During quench, both deposit and plate contract and the differential contraction of the different metals of which deposit and plate consist, produces stresses at the interface between the deposit and the plate. Since adhesion

is at least in part due to mechanical keying, separation of at least portions of the interface is produced by the inter-action of stresses resulting from differential contraction and stresses produced in the deposit during deposition. Some degree of thermal shock is desired to achieve good separation.

Since the deposit adheres to the whole of the immersed surface of the cathode plate, it is an advantage to separate the deposit on one side of the plate from that on the other side by masking at least one of the edges. Preferably both side edges are masked with a non-conducting material such as a plastics or elastomeric beading. One edge, preferably the lower edge in relation to the suspension of the plate, may be provided with a V-shaped longitudinal groove to assist in effecting separation of the deposits.

After quenching, the deposit may in some cases separate from the plate, but in other cases reheating to a temperature up to that of the electrolytic bath is necessary to effect separation. Where the surface of the plate is smooth and a plastic edging is used on the plate, copper will separate from a titanium plate on cooling but if the surface of the plate is roughened, for example, by abrasion, reheating has been found to be necessary. Full scale trials on stripping copper from titanium have indicated that it is necessary to quench and reheat even on nominally smooth surfaced plates.

It is believed that deposit is held on the plate by mechanical keying and by compressive forces perpendicular to the titanium plate. The deposit and the plate constitute a couple and during cooling from the temperature of the plating bath the stress will increase as long, as each member of the couple deforms elastically. When the elastic limit of one member of the couple is exceeded, plastic deformation will ensue and relieve the strain. Therefore, for stripping to occur, it is necessary that the bond between the two members of the couple should be broken before this point is reached. Once the bond has been broken in planar regions of the surface, the deposit may be retained by mechanical keying with the plate. As the deposit between the mechanical keys cools, it is possible that "pinching" occurs and reheating relieves this mechanical effect and permits removal of the deposit. Thermal cycling also has the effect of fatiguing the keying metal which will facilitate fracture during stress reversal.

The invention is applicable not only to copper deposits on titanium cathode plates, but also to other combinations of metals, for example, zinc deposit on aluminium, nickel deposit on stainless steel or on titanium.

An advantage of the method according to the invention is that only simple and inexpensive modifications of the existing process are required, such as th eprovision of a quench tank and cooling facilities for the coolant liquid and means for reheating, such as a hot water tank. Instead of a manual or mechanical stripping facility, means may be required in the quench tank or the reheating tank or oven to collect the deposits as they become detached from the plate. Where there are no means of providing separation between the deposits on each face of the plates, such as plastic edging or grooving of the plate, a manual operation may be necessary at the edges before the deposits detach themselves from the plates.

WHAT WE CLAIM IS:-

1. A method of removing an electrodeposit of metal adhering, to a flat cathode plate of a metal of dissimilar coefficient of thermal expansion including the steps of subjecting the deposit and the cathode plate to a temperature change thus creating a thermal expansion or contraction differential between the deposit and the cathode plate, whereby the resulting stresses generated at the interface between the deposit and the cathode plate are sufficiently great to reduce adhesion between the deposit and the cathode plate.

2. A method as claimed in claim 1 in which a temperature change of about 60°C is achieved.

3. A method as claimed in claim 1 or claim 2 in which the temperature change is effected by quenching the cathode plate and deposit from the electrodeposition temperature using a liquid bath or at below ambient temperature.

4. A method as claimed in claim 3 in which the liquid bath is chilled to about 0°C.

5. A method as claimed in Claim 1 or claim 2 in which the temperature change is effected by cooling the cathode plate and deposit from the electrodeposition temperature using air at or below ambient temperature.

6. A method as claimed in claim 1 or claim 2 in which the temperature change is effected by cooling the cathode plate and deposit from the electrodeposition temperature using solid carbon dioxide.

7. A method as claimed in claim 1 or claim 2 in which the temperature change is effected by heating the cathode plate and deposit from the electrodeposition temperature using water at or near its boiling point.

8. A method as claimed in any one of claims 1 to 6 in which the cathode plate and deposit after quenching or otherwise cooling are reheated.

9. A method as claimed in claim 8 in which the cathode plate and deposit after reheating are again quenched or otherwise cooled.

10. A method as claimed in claim 7 in which the cathode plate and deposit after heating are quenched or otherwise cooled.

11. A method as claimed in any one of claims 1 to 3 or 5 to 7 in which the cathode plate and deposit are removed from the electrodeposition bath and transferred to an environment of 60 - 70°C prior to quenching or

otherwise cooling.

12. A method as claimed in claim 11 in which the cathode plate and deposit are immersed in water at 60 - 70°C to effect rinsing of the deposit.

13. A method as claimed in any one of the preceding claims in which the cathode plate is of titanium, stainless steel or aluminium.

14. A method as claimed in any one of claims 1 to 12 in which the deposit is of copper, zinc or nickel.

15. A method as claimed in any one of claims 1 to 13 in which the cathode plate is provided on at least one of its edges with a mask of non-conducting material.

16. A method as claimed in any one of claims 1 to 13 or 15 in which the lower edge of the cathode when in the suspended position is provided with a V-shaped longitudinal groove

17. A method of removing an electrodeposit from a cathode plate substantially as hereinbefore described with reference to any one of the preceding claims.

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